

were computed on the basis of 7.0 lbs of meat to the bushel. However, the factor was determined or redetermined that year and found to vary from 3.23 for Alabama oysters to 4.65 for Texas oysters. Since then, the Federal reports generally give this computing factor for each state for the years reported, because the factor also varies from year to year for each state. For the State of Louisiana it varied from 4.09 to 5.59 in the 5 years reported between 1932 and 1940, averaging 4.57 lbs to the bushel. This means that the Federal statistics for the State of Louisiana, in pounds, are approximately 35% exaggerated for all years previous to 1931. It explains why Louisiana's oyster production in pounds, as given in the Federal reports, shows a much greater variance from the State of Louisiana barrel figures before 1930 than afterwards. However, when the proper computing figures are used for turning the Federal figures into barrels produced, it is found that the annual oyster production of Louisiana, as given by the State and Federal Governments from 1911 to 1945 for the 16 comparable years in that period, differs only by 20,181 barrels or approximately 3%, the Federal figure being the greater.

According to the pounds figures of the Federal Government, the State of Louisiana produced 10 times as much oysters in 1911 as in the lowest depression year, 1932.

Possibly this situation is the cause for misgivings concerning Louisiana's oyster industry, viz. Chipman (Oyster Institute of North America Trade Report No. 91, June 1948; mimeographed): "... the mortality of oysters in Louisiana waters threatens the very existence of the large oyster industry of that state." However, the misgivings are unfounded, for the State of Louisiana statistics and properly interpreted Federal statistics show that there has been no major decline in Louisiana's oyster production since 1905, when the industry got under way. A complete analysis will be given elsewhere.

Unfortunately, the same thing cannot be said of other Gulf States. Taken together, they produced 952,000 barrels of oysters a year in the 1920s, 395,000 in the '30s, and 209,000 in the '40s. This decline is clear, indubitable, and huge.

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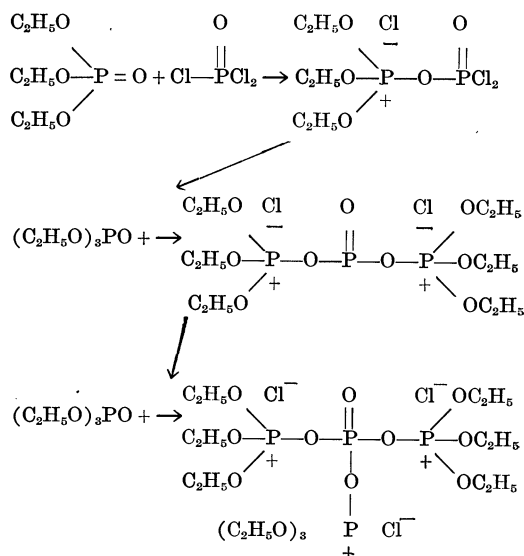
## Some Views on the Phosphorylation Reactions

Although several years have passed since the introduction of polyphosphate esters as insecticides, no investigations have been made public in which the nature of the products or the mode of their formation from phosphorus oxychloride and, for example, triethyl phosphate has been studied. The patents under which these compounds were disclosed (Ger. 720,577 and U.S. 2,336,302; to I. G. Farbenindustrie) represent the reaction of formation of "hexaethyl tetraphosphate" as substitution of chlorine atoms by diethylphosphoryl groups, giving the final product a symmetrical pyramidal structure.

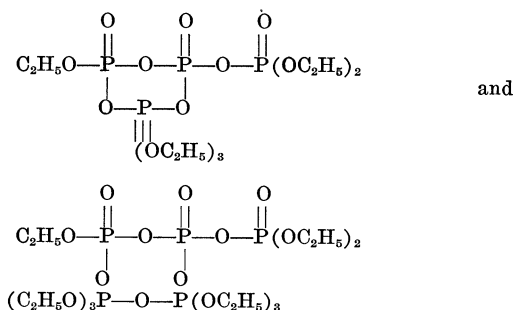
Determinations of molecular weights of reaction products of three moles of triethyl phosphate with one mole

of phosphorus oxychloride in accordance with the patent disclosures showed that the actual molecular weights range from 560 to over 700 (freezing point, in benzene); that is to say, they are considerably in excess of the theoretical value (506) required by the pyramidal formulation. In addition, the infrared absorption spectra of such products reveal a close similarity to the spectra of ethyl metaphosphate esters, characterized by a wide and intense band near  $10\ \mu$ .

Correlation of these observations with the known hydrogen bonding tendency of trialkyl phosphates, as shown by Audrieth and Steinman (*J. Amer. chem. Soc.*, 1941, 63, 2115), leads to the possibility of the following representation of the nature of the reaction and of the resulting products, on the basis of addition reactions to the PO bond of the triethyl phosphate, giving intermediate "phosphonium type" adducts, which are capable, at each step, of formation of linear polyesters or of cyclic polyesters by thermal decomposition analogous to that of the thermal cleavage of true phosphonium compounds. The complexity of possibilities at each step merely confirms the complex nature of the final product.

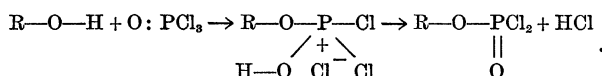


It will be noted that the intermediates can decompose either "intragroup" (losing ethyl chloride) or they can react with a group in another part of the molecule by an "intergroup" reaction. Carrying the scheme to its logical conclusion, one arrives at structures shown below:



The formation of such high-molecular-weight cyclic compounds explains both the high molecular weights observed for such products and the type of infrared spectra exhibited by them. Even larger molecules can be visualized by extending the above representation further. In addition, a similar formulation serves to explain the formation of apparently identical substances by the interaction of phosphorus pentoxide with triethyl phosphate (Adler and Woodstock. *Chem. Industr.*, 1942, 516).

The concept of addition reactions to the PQ linkage has been mentioned by Gerrard (*J. chem. Soc.*, 1945, 106) as a possible mode of reaction of alcohols with phosphorus oxychloride, through an intermediate adduct of a type ROH . . . OPCl<sub>3</sub>. It is possible, however, to modify this concept and to formulate such a reaction by



means of a "phosphonium type" mechanism similar to that used above.

Such a formulation, in so far as known, is not contrary to known facts about the interaction of phosphorus oxychloride with primary alcohols and may serve as a bridge between the chemistry of the pentavalent phosphorus compounds and the chemistry of trivalent phosphorus

compounds, where the formation of "phosphonium type" adducts has been observed in numerous cases. The actual formation of an adduct between an alcohol and phosphorus oxychloride has been shown by the determination of molecular weights of equimolecular mixtures of *n*-octanol and phosphorus oxychloride in benzene at 3-4° C. Within 5 min of addition the average molecular weight was found to be 186.3; 1 hr later the value rose to 195.5, indicating a slow and steady accumulation of an adduct. After 1 hr the mixture began to evolve hydrogen chloride (which may be formulated as given above), and the value of the average molecular weight obviously began to drop. This appears to be the first instance of detection of an adduct of an alcohol with phosphorus oxychloride. Attempts to use alcohols of lower molecular weights gave

mixtures in which the evolution of hydrogen chloride began at much lower temperatures, such as to preclude reliable measurements with conventional solvents.

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## Why Vegetation on Watersheds?

"Save our forests and humus to conserve our water supply." "Forest and brush fires will deplete our water supply." These and similar slogans have given the public an erroneous idea of the relation between a storage reservoir and vegetation.

The following remarks apply only to the strictly utilitarian but vital problem of watersheds which drain into storage reservoirs of sufficient size to hold the entire annual precipitation. There exists among the laity a misunderstanding engendered by numerous articles which have not stressed the wide difference between water storage and undammed rivers.

A storage reservoir is just what its name implies—a dam across a drainage artery to conserve the run-off from its watershed, for subsequent distribution to consumers. Is vegetation on such a watershed of value in the sense in which it is ordinarily understood, or is its chief value altogether different?

If you lived in southern California, or in a location with similarly distributed rainfall, and had a large cistern for catching rainwater from your roof, you could estimate your approximate annual storage, if you knew the area of your roof and the average amount of rainfall. Your roof may be likened to a watershed and your cistern to a storage reservoir. Your roof is devoid of vegetation, but you understand that vegetation is vital to your community's watershed and storage reservoir. Therefore, if you are consistent, you should hasten to cover your roof with boxes filled with leaf mold or humus supporting a luxuriant growth of plants to "conserve your water supply." The plants and humus on your roof will do exactly what they would do on your community watershed, namely,

catch and hold part of the water that would have gone into your cistern. The luxuriant plants gradually absorb much of it and breathe it out into the atmosphere. The remainder evaporates from the surface of the humus, except for a little which has been delayed and gradually seeps out of the boxes, but most of this seepage evaporates before reaching your cistern.

Looked at in this light, it is evident that vegetation on a watershed draining into a storage reservoir causes a waste of water. The evaporation from the surface of the impounded lake is but a fraction of the loss sustained by the evaporation from vegetation and from the "delayed" water which gradually seeps toward the reservoir, but is largely lost by capillarity and the ensuing evaporation. Therefore, vegetation on a watershed is a detriment in so far as saving all the water that falls is concerned.

As one sails among the West Indies, or other places that suffer from protracted droughts, one notes large white areas on the hillsides above the towns. These are water-catching areas that drain into reservoirs. The authorities would no more think of covering them with vegetation than you would your roof from which you expected to fill your cistern. How do these catchment areas differ from the watershed of your community? The white areas are solid cement pavement—very rough, unadorned, and purely utilitarian, but very effective.

Now we come to the real and vital need for vegetation on our watersheds. It is purely mechanical. If there is erosion, the reservoir will fill with detritus and you will be without storage space. If you could have your watershed covered by "gunnite" or paved, you could recover all but a negligible fraction of the rainfall. Therefore, the only use of vegetation on your watershed is to hold